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CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

Using Third-Generation CALPHAD Models to Approximate Thermodynamic Properties of Solid Uranium Diboride

A. L. Voskov[a],*

[a] *Faculty of Chemistry, Moscow State University, Moscow, 119991 Russia*
**e-mail: alvoskov@gmail.com*

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Abstract—Expressions are obtained for the Gibbs energy of solid uranium diboride UB_2 at $T = 0–2300$ K in the standard element reference system. They are established to describe the experimental data on heat capacity and heat content throughout the range of temperatures with a single dependence. The weighted sum of the Einstein functions with no polynomial contribution is shown to approximate the limit behavior of the heat capacity at $T = 1–5$ K. A simplified dependence with six parameters is proposed for the Gibbs energy at $T = 200–2000$ K.

Keywords: uranium diboride, heat capacity, heat content, Einstein functions, Gibbs energy, enthalpy, CALPHAD

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INTRODUCTION

Uranium diboride UB_2 is of interest as a component of promising nuclear fuels resistant to accidents (accident tolerant fuels) [1]. Studies of its thermodynamic properties are important both for optimizing the conditions for fuel production and for predicting phase and chemical equilibria with its participation. The thermodynamic model of a uranium–boron binary system in [2] allows us to obtain the phase diagram and the properties of all binary compounds in it: UB_2, UB_4, and UB_{12}. It belongs to the second-generation CALPHAD models; i.e., it is based on polynomial functions and can be used only when $T \geq 298.15$ K. A possible alternative is the third-generation CALPHAD models first proposed in 1995 [3]. The Einstein or Debye functions are used in these models to approximate isobaric heat capacity C_p, ensuring their applicability down to 0 K and the possibility of extrapolating them to both low and high temperatures. Voronin and Kutsenok [4] and Jacobs et al. [5] independently proposed using the weighted sum of several Einstein functions to achieve high accuracy in approximating the heat capacity of complex substances in a wide range of temperatures. This model was supplemented with a polynomial in [6] and used to approximate the heat capacities of graphite and diamond.

There are experimental data on isobaric heat capacity C_p [7] and heat content $H_T - H_{298.15}$ [8, 9] for solid uranium diboride UB_2 that cover the 1.1–2300 K range of temperatures. A brief list of these is presented in Table 1. All were obtained for samples of composition $UB_{1.979}$. To move to thermodynamic functions of stoichiometric UB_2, we used factor $3/2.979 \approx 1.007$ proposed in [7]. Values of the thermodynamic functions of UB_2 at $T = 298.15$ K, obtained from experimental data on heat capacity, were recommended in that work: $S^\circ_{298.15} = 55.51 \pm 0.11$ J/(mol K), $H^\circ_{298.15} - H^\circ_0 = 8880 \pm 17$ J/mol, and $C^\circ_{p,298.15} = 55.76 \pm 0.11$ J/(mol K).

The enthalpy of formation of uranium diboride $\Delta_f H^\circ_{298.15}(UB_2) = -164.43 \pm 17$ kJ/mol (-39.3 ± 4.0 kcal/mol) [7] was obtained by burning a UB_2 sample in a fluorine atmosphere inside a calorimetric bomb, and using literature data on the enthalpies of formation of UF_6 and BF_3.

The temperature dependence of the Gibbs energy for UB_2 at $T = 298.15–2300$ K [2] in the standard element reference system is presented along with experimental data. The formulas are given in terms of $U_{1/3}B_{2/3}$:

$$\begin{aligned} G(T) - H_{\mathrm{SER}},\ \mathrm{J/mol} &= -63972.50 \\ &+ 137.55038T - 22.286574T\ln T \\ &- 5.157738\times10^{-3}T^2 + 0.39417\times10^{-6}T^3 \\ &+ 310100/T \quad (298.15 < T < 1600\ \mathrm{K}), \end{aligned} \tag{1}$$

$$\begin{aligned} G(T) - H_{\mathrm{SER}},\ \mathrm{J/mol} &= -344980.46 \\ &+ 2063.58552T - 283.582964T\ln T \\ &+ 106.066517\times10^{-3}T^2 - 8.73248\times10^{-6}T^3 \\ &+ 58632007/T \quad (1600 < T < 2300\ \mathrm{K}), \end{aligned} \tag{2}$$

Table 1. Available experimental data on heat capacities and heat contents of UB_2

T, K	Type of data	Number of points	Measuring technique	Reference
1.1–20.6	C_p	41	Isoperibol calorimetry	[7]
7.4–348	C_p	55	Adiabatic calorimetry	[7]
579–1486	$H_T - H_{298.15}$	18	Drop calorimetry	[8]*
1303–2300	$H_T - H_{298.15}$	11	Drop calorimetry	[9]*

* Experimental data on heat content $H_T - H_{298.15}$, recalculated for the stoichiometric composition of UB_2, were taken from [2].

where H_{SER} is the reference level, i.e., the enthalpies of formation of simple substances (stable allotropic modifications) at $T = 298.15$ K and $p = 1$ bar. The generalized $G_T - H_{\mathrm{SER}}$ expression for an individual compound is

$$G_T - H_{\mathrm{SER}} = (H_T - H_{298.15} + \Delta_f H^\circ_{298.15}) - TS_T, \quad (3)$$

where $\Delta_f H^\circ_{298.15}$ is the standard enthalpy of formation. For UB_2, we used the value obtained for it in [7] (see above). Disadvantages of this polynomial model are the use of two different dependences for $T = 298.15$–1600 and >1600 K, along with its unsuitability for calculating C_p at $T < 298.15$ K. Entropy $S^\circ_{298.15} = 54.525$ J/(mol K) was used as is (i.e., it cannot be obtained from the $C_p(T)$ polynomial dependence).

No thermodynamic models that allow us to calculate isobaric heat capacity of UB_2 at $T = 0$–298.15 K are described in the literature. The following approximation of low-temperature C_p for $T < 4.2$ K was proposed in [7]:

$$C_p, \text{ mJ/(mol K)} = (9.40 \pm 0.01)T + (3.18 \pm 0.14) \times 10^{-2} T^3. \quad (4)$$

An approximation of the heat capacity anomaly of solid UB_2 at $T = 40$–100 K, made using a two-level Schottky model, was proposed in the same work. Unfortunately, these two models do not cover the entire 0–298.15 K range of temperatures and cannot be used to calculate $S^\circ_{298.15}$. While the experimental heat capacities were approximated in [7] by polynomial dependences, the dependences themselves are not given.

The aim of this work was to obtain the temperature dependences of the Gibbs energy of solid uranium diboride UB_2, based on the third-generation CALPHAD models and the available experimental data on isobaric heat capacity, heat content, and enthalpy of formation.

CALCULATIONS

Experimental data on heat capacity and heat content were approximated using a model that included a weighted sum of Einstein functions and a polynomial contribution:

$$C_p(T, \boldsymbol{\alpha}, \boldsymbol{\theta}, a_1, a_2) = \sum_{i=1}^{m} \alpha_i C_{\mathrm{E}}\left(\frac{\theta_i}{T}\right) + Ra_1\left(\frac{T}{T_0}\right) + Ra_2\left(\frac{T}{T_0}\right)^4, \quad (5)$$

$$\frac{C_{\mathrm{E}}(x)}{R} = \frac{3x^2 e^x}{(e^x - 1)^2}, \quad (6)$$

where $T_0 = 298.15$ K; R is the universal gas constant; m is the number of Einstein functions; and α_i, θ_i, a_1, and a_2 are model parameters. This model was proposed in [6] and obtained by adding a polynomial to the model of isobaric heat capacity proposed by Voronin and Kutsenok in [4] and based on the weighted sum of Einstein functions. The polynomial of Eq. (5) differs from the $AT + BT^4$ expression used in [6] by dimensionless coefficients a_1 and a_2.

The expressions for entropy and heat content can be obtained by integrating Eq. (6):

$$S(T, \boldsymbol{\alpha}, \boldsymbol{\theta}, a_1, a_2) = \sum_{i=1}^{m} \alpha_i S_{\mathrm{E}}\left(\frac{\theta_i}{T}\right) + Ra_1\left(\frac{T}{T_0}\right) + \frac{Ra_2}{4}\left(\frac{T}{T_0}\right)^4, \quad (7)$$

$$\frac{S_{\mathrm{E}}(x)}{R} = 3\left(\frac{x}{e^x - 1} - \ln(1 - e^{-x})\right), \quad (8)$$

$$H(T, \boldsymbol{\alpha}, \boldsymbol{\theta}, a_1, a_2) - H_0 = \sum_{i=1}^{m} \alpha_i H_{\mathrm{E}}\left(\frac{\theta_i}{T}\right) + RT\left(\frac{a_1}{2}\left(\frac{T}{T_0}\right) + \frac{a_2}{5}\left(\frac{T}{T_0}\right)^4\right), \quad (9)$$

$$\frac{H_{\mathrm{E}}(x)}{RT} = \frac{3x}{e^x - 1}. \quad (10)$$

The expression for the Gibbs energy in the standard element reference system can be obtained by substituting Eqs. (7)–(10) into Eq. (3):

$$\begin{aligned} G(T,\boldsymbol{\alpha},\boldsymbol{\theta},a_1,a_2) - H_{\mathrm{SER}} &= \Delta_{\mathrm{f}}H^{\circ}_{298.15} \\ &- (H_{298.15} - H_0) + \sum_{i=1}^{m}\alpha_i G_{\mathrm{E}}\left(\frac{\theta_i}{T}\right) \\ &- RT\left(\frac{a_1}{2}\left(\frac{T}{T_0}\right) + \frac{a_2}{20}\left(\frac{T}{T_0}\right)^4\right), \end{aligned} \tag{11}$$

$$\frac{G_{\mathrm{E}}(x)}{RT} = \frac{H_{\mathrm{E}}(x)}{RT} - \frac{S_{\mathrm{E}}(x)}{R} = 3\ln(1 - e^{-x}). \tag{12}$$

Four versions of the above model were used to approximate experimental data.

The first was model Ein with no polynomial (i.e., $a_1 = a_2 = 0$ in Eqs. (5), (7), (9), and (11)), the parameters of which were obtained using all of the experimental data in Table 1.

The second was model EinLT with no polynomial. Only data on interval $T = 0$–1486 K were used in optimizing its parameters.

The third was model EinPoly with a polynomial (i.e., $a_1 \neq 0$ and $a_2 \neq 0$) based on the same data as model Ein.

The fourth was simplified model Ein2 with two Einstein functions and a polynomial based on the data for $T = 200$–2300 K, along with values $S^{\circ}_{298.15}$ and $H^{\circ}_{298.15} - H^{\circ}_0$ obtained using model Ein.

The model parameters were optimized using nonlinear least squares in the CpFit program [10]. An objective function based on a weighted sum of the squares of relative deviations was used for the first three models:

$$\begin{aligned} RSS &= \sum_{k=1}^{n_C}\omega_{C,k}^2\left(\frac{C_p^{\mathrm{calc}}(T_k) - C_{p,k}^{\mathrm{exp}}}{C_{p,k}^{\mathrm{exp}}}\right)^2 \\ &+ \sum_{k=1}^{n_H}\omega_{H,k}^2\left(\frac{\Delta H^{\mathrm{calc}}(T_k) - \Delta H_k^{\mathrm{exp}}}{\Delta H_k^{\mathrm{exp}}}\right)^2, \end{aligned} \tag{13}$$

where indices calc and exp denote calculated and experimental values, and ω_C and ω_H are the statistical weights for isobaric heat capacities and heat contents, respectively: $\omega_C = 1$ for $T \geq 5$ K and $\omega_C = 0.25$ for $T < 5$ K. Unit statistical weights of $\omega_H = 1$ were used in all models except Ein2, where $\omega_H = 1$ and 0.1 for points from [8] ($T = 479$–1486 K) and [9] ($T = 1303$–2300 K), respectively. For simplified model Ein2 with two Einstein functions and a polynomial, experimental data were used exclusively for $T > 100$ K. The reproducibility of $S^{\circ}_{298.15}$ and $H^{\circ}_{298.15} - H^{\circ}_0$ was ensured by introducing two additional terms into the objective function (i.e., using a new RSS_2 objective function):

$$\begin{aligned} RSS_2 &= RSS + 10^4\left(\frac{S^{\mathrm{o,calc}}_{298.15} - S^{\mathrm{o,ref}}_{298.15}}{S^{\mathrm{o,ref}}_{298.15}}\right)^2 \\ &+ 10^4\left(\frac{\Delta H^{\mathrm{o,calc}} - \Delta H^{\mathrm{o,ref}}}{\Delta H^{\mathrm{o,ref}}}\right)^2, \end{aligned} \tag{14}$$

where RSS is the objective function described by Eq. (13), and superscripts calc and ref refer to values obtained from models Ein2 and Ein, respectively. When optimizing the parameters of model Ein2, additional condition $\sum_i \alpha_i = N_{\mathrm{atoms}} = 3$ implemented in the CpFit program by a change of variables was used as well:

$$\begin{cases} \alpha_1 = (1 - \xi_1)N_{\mathrm{atoms}} \\ \alpha_2 = \xi_1 N_{\mathrm{atoms}}, \end{cases} \tag{15}$$

where $\xi_1 \in [0;\, 1]$ is the parameter to be optimized, and $N_{\mathrm{atoms}} = 3$.

Two values were used to estimate the accuracy of the experimental data approximation: the standard deviation and the normalized median absolute deviation. They were calculated for the absolute and relative deviations as

$$\begin{aligned} s(\delta Y) &= \sqrt{\frac{\sum_{i=1}^{n}(Y_i^{\mathrm{calc}} - Y_i^{\mathrm{exp}})^2}{n}}; \\ s(\varepsilon Y) &= \sqrt{\sum_{i=1}^{n} n^{-1}\left(\frac{Y_i^{\mathrm{calc}} - Y_i^{\mathrm{exp}}}{Y_i^{\mathrm{exp}}}\right)^2}; \end{aligned} \tag{16}$$

$$\begin{aligned} s_{\mathrm{MAD}}(\delta Y) &= \frac{\mathrm{median}\left|Y_i^{\mathrm{calc}} - Y_i^{\mathrm{expt}}\right|}{\Phi^{-1}(0.75)}; \\ s_{\mathrm{MAD}}(\varepsilon Y) &= \frac{\mathrm{median}\left|\dfrac{Y_i^{\mathrm{calc}} - Y_i^{\mathrm{expt}}}{Y_i^{\mathrm{expt}}}\right|}{\Phi^{-1}(0.75)}, \end{aligned} \tag{17}$$

where Y is isobaric heat capacity C_p or heat content $H_T - H_{298.15}$, and $\Phi^{-1}(x)$ is the inverse cumulative distribution function for standard normal distribution $1/\Phi^{-1}(0.75) \approx 1.483$. A more detailed description of these estimates of the accuracy of approximation, including the rationale for using normalizing factor 1.483, was given in [11] on the use of the CpFit program for compiling databases.

Table 2. Optimized model parameters α_i, θ_i, a_1, and a_2 for the weighted sum of Einstein functions with and without a polynomial (see Eqs. (5), (7), (9), and (11))

Parameter	Model		
	Ein	EinLT	EinPoly
α_1	248.427 ± 460	0.753366 ± 0.080	1.36636 ± 0.33
θ_1, K	20583.0 ± 4800	2566.79 ± 360	1054.84 ± 86
α_2	0.748971 ± 0.081	1.98150 ± 0.094	0.918373 ± 0.33
θ_2, K	2525.86 ± 360	865.288 ± 45	622.662 ± 64
α_3	1.98367 ± 0.092	0.295821 ± 0.12	0.903728 ± 0.0099
θ_3, K	861.749 ± 46	411.299 ± 93	179.195 ± 2.1
α_4	0.287805 ± 0.11	0.900898 ± 0.027	0.0695765 ± 0.012
θ_4, K	405.253 ± 96	175.593 ± 2.2	98.1887 ± 4.2
$10^3\alpha_5$	899.380 ± 29	61.9041 ± 11	2.42919 ± 0.40
θ_5, K	175.441 ± 3.4	90.8470 ± 4.8	34.2918 ± 2.2
$10^3\alpha_6$	61.4672 ± 12	5.8325 ± 0.58	0
θ_6, K	90.6821 ± 5.1	33.0569 ± 2.8	0
$10^3\alpha_7$	5.8178 ± 0.60	1.5352 ± 0.24	0
θ_7, K	33.0007 ± 2.9	11.846 ± 1.6	0
$10^3\alpha_8$	1.5315 ± 0.25	0.74844 ± 0.11	0
θ_8, K	11.8263 ± 1.6	3.0199 ± 0.43	0
$10^3\alpha_9$	0.74745 ± 0.11	0	0
θ_9, K	3.01636 ± 0.45	0	0
a_1	0	0	0.345204 ± 0.0035
a_2	0	0	$(9.1395 \pm 1.3) \times 10^{-4}$
$\sum_i \alpha_i$	252.4	4.002	3.260

Table 3. Accuracy of approximating experimental data on heat capacity from [7] (see Table 1) using different models

Model	T, K	$100s(\varepsilon C_p)$	$100s_{\mathrm{MAD}}(\varepsilon C_p)$	$s(\delta C_p)$, J/(mol K)	$s_{\mathrm{MAD}}(\delta C_p)$, J/(mol K)
Ein	1.1–20.6	0.56	0.76	8.8×10^{-4}	2.3×10^{-4}
	7.4–348	0.58	0.28	0.079	0.031
EinLT	1.1–20.6	0.56	0.78	8.9×10^{-4}	2.3×10^{-4}
	7.4–348	0.58	0.28	0.078	0.032
EinPoly	1.1–20.6	0.78	1.0	8.9×10^{-4}	3.2×10^{-4}
	7.4–348	0.58	0.23	0.048	0.037
Ein2	200–348	0.23	0.28	0.11	0.15
Poly	298–348	1.1	1.1	0.63	0.65

Table 4. Accuracy of approximating experimental data on heat content from [8, 9] (see Table 1) using different models

Model	T, K	$100s(\varepsilon\Delta H)$	$100s_{\mathrm{MAD}}(\varepsilon\Delta H)$	$s(\delta\Delta H)$, kJ/mol	$s_{\mathrm{MAD}}(\delta\Delta H)$, kJ/mol
Ein	579–1486	0.22	0.23	0.13	0.15
	1303–2300	0.42	0.55	0.51	0.64
EinLT	579–1486	0.22	0.23	0.14	0.13
	1303–2300	3.6	1.0	6.5	1.1
EinPoly	579–1486	0.40	0.50	0.24	0.29
	1303–2300	0.94	0.91	1.4	1.2
Ein2	579–1486	0.29	0.27	0.16	0.16
	1303–2300	1.5	0.82	2.7	1.2
Poly	579–1486	0.26	0.17	0.087	0.12
	1303–2300	0.57	0.27	0.72	0.39

RESULTS AND DISCUSSION

The resulting sets of parameters for Eqs. (5)–(12) are presented in Table 2. The parameters below were obtained for simplified model Ein2:

$$\begin{gathered}\alpha_1 = 1.96081, \quad \alpha_2 = 1.03919,\\ \theta_1/\mathrm{K} = 855.158, \quad \theta_2/\mathrm{K} = 181.689, \\ a_1 = 0.609182, \quad a_2 = 1.88976\times10^{-5}.\end{gathered} \tag{18}$$

Tables 3 and 4 show the accuracy of approximating experimental data on isobaric heat capacity [7] and heat content [8, 9] using different thermodynamic models: those obtained in this work and taken from [1]. The two temperature ranges in the data from [7] correspond to samples obtained by isoperibol and adiabatic calorimetry (see Table 1).

Figures 1 and 2 show results from approximating experimental data on isobaric heat capacity and heat content. The temperature dependences of C_p and $H_T - H_{298.15}$ are shown in Figs. 1a and 2a, and the corresponding scatter plots are shown in Figs. 1b and 2b.

Files of the initial data and obtained model parameters are available at https://doi.org/10.17632/3vkpz6nfff.1 as the Mendeley Data Set for the CpFit and GNU Octave programs for plotting and tables.

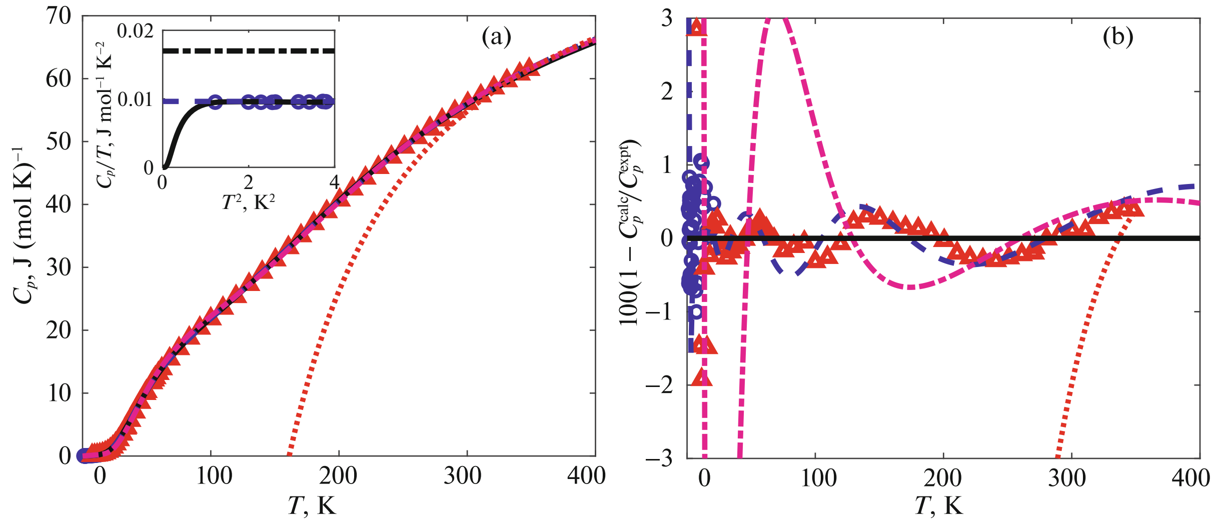

Fig. 1. Results from approximating experimental values of the isobaric heat capacity of UB_2: (a) dependences of C_p on T; (b) dependences of relative deviations $\varepsilon C_p = 100(C_p^{\mathrm{expt}} - C_p^{\mathrm{calc}})/C_p^{\mathrm{expt}}$ on T. The solid, dashed, dashed-and-dotted, and dotted lines are models Ein, EinPoly, Ein2, and Poly, respectively. Dots are experimental values of C_p from [7]; rings and triangles are data from isoperibol and adiabatic calorimetry, respectively.

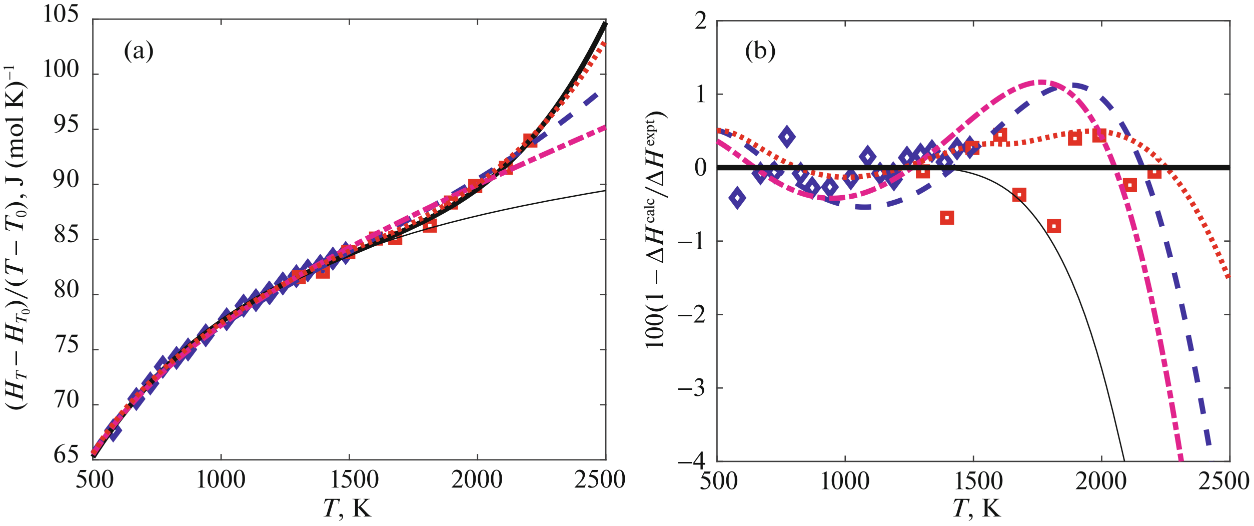

Fig. 2. Results from approximating experimental values of the heat content of UB_2: (a) the dependence of $\Delta H = (H_T - H_{T_0})/(T - T_0)$ on T, $T_0 = 298.15$ K; (b) the dependence of relative deviations $\varepsilon\Delta H = 100(\Delta H^{\rm expt} - \Delta H^{\rm calc})/\Delta H^{\rm expt}$ on T. The bold, fine, dashed, dashed-and-dotted, and dotted lines show data obtained using models Ein, EinLT, EinPoly, Ein_2, and Poly, respectively. Dots are experimental data obtained via drop calorimetry; diamonds and squares are values from [8] and [9], respectively.

Model Ein with nine Einstein functions and no polynomial with 18 optimized parameters turned out to be the most accurate of those obtained in this work. In it, $\sum_i \alpha_i \gg N_{\rm atoms} = 3$. This because with no polynomial, difference $C_p - C_V$, the anharmonicity of lattice vibrations, and the growth of C_p before melting are approximated by Einstein functions with values of α_i and θ_i, which have no explicit physical meaning. This was observed in [10] for uranium dioxide UO_2.

Adding a polynomial to model EinPoly allowed us to approximately meet condition $\sum_i \alpha_i \approx N_{\rm atoms}$ for UB_2 and reduce the number of Einstein functions to five, and the number of model parameters to 12 (Table 2). It also improved the limit behavior of the model at $T < 1$ K (see Fig. 1a). Models Ein and EinPoly in this case have comparable accuracy throughout the $T = 1$–2300 K range of temperatures, and the differences when $T < 1$ K do not affect the values of $S^\circ_{298.15}$ and $H_T - H_{298.15}$ appreciably. Condition $\sum_i \alpha_i \approx N_{\rm atoms} = 3$ was met approximately for model EinLT by excluding data on heat content when $T >$ 1486 K. This allowed us to reduce the number of Einstein functions to eight, and the number of parameters to 16. It also reduced the accuracy of approximating the experimental values of $H_{\rm T} - H_{298.15}$ from [8] ($T =$ 1303–2300 K).

Models Ein, EinLT, and EinPoly obtained in this work describe the heat capacity of UB_2 more accurately than the polynomial model available in [2]. They are not inferior to it in terms of approximating heat content, but the first two require more optimized parameters. The polynomial model in [2] has only 12 parameters: six for each temperature interval (see Eqs. (1) and (2)). To test the possibility of reducing their number, we constructed simplified model Ein2 with six parameters that included two Einstein functions and a polynomial. Its accuracy was comparable to models Ein, EinLT, and EinPoly at $T =$ 200–2000 K with fewer parameters. Its accuracy fell notably outside this range (see Figs. 1, 2), but the values it produced remained physically correct.

The tabulated values of the thermodynamic functions of solid uranium diboride UB_2 when $T =$ 1–2300 K are given in Table 5. They were calculated using model Ein (i.e., the one based on the weighted Einstein function with no polynomial), since it was more accurate than the others, including the polynomial model described in [2]. The values of $C^\circ_{p,298.15}$, $S^\circ_{298.15}$, and $H_T - H_{298.15}$ obtained from all four models constructed in this work coincided within their confidence intervals. They also agreed with the data in [7].

CONCLUSIONS

Thermodynamic models based on the weighted sum of Einstein functions allowed us to approximate experimental data on the heat capacity and heat content of solid uranium diboride throughout the 1–2300 K range of temperatures. Adding a polynomial of the $AT + BT^4$ form to dependence $C_p(T)$ did not improve the accuracy of approximation. However, it did reduce the number of model parameters, allowed

Table 5. Thermodynamic functions of uranium diboride UB_2, calculated using model Ein (see Eqs. (5), (7), (9), (11), and their parameters in Table 2)

T, K	C_p, J/(mol K)	S, J/(mol K)	$H - H_0$, J/mol	$G - H_{SER}$, J/mol
1	9.2×10^{-3}	3.8×10^{-3}	2.9×10^{-3}	−173 315
5	0.051	0.043	0.12	−173 315
10	0.13	0.10	0.56	−173 316
20	0.79	0.33	4.16	−173 317
50	10.30	4.32	157.13	−173 374
100	21.89	15.47	994.40	−173 867
150	31.03	26.04	2313.5	−174 907
200	40.62	36.29	4106.3	−176 466
250	49.10	46.29	6355.8	−178 532
298.15	55.72 ± 0.16	55.53 ± 0.10	8885.1 ± 17	−180 985
300	55.94	55.87	8988.4	−181 089
350	61.40	64.92	11 926.9	−184 111
400	65.83	73.42	15 111.3	−187 571
500	72.68	88.89	22 055.4	−195 703
600	77.77	102.6	29 589.6	−205 291
700	81.67	114.9	37 569.9	−216 177
800	84.71	126.0	45 895.1	−228 232
900	87.09	136.1	54 489.7	−241 347
1000	88.99	145.4	63 297.2	−255 431
1100	90.52	154.0	72 274.8	−270 405
1200	91.79	161.9	81 391.8	−286 204
1300	92.94	169.3	90 628.6	−302 768
1400	94.11	176.2	99 979.9	−320 047
1500	95.53	182.8	109 459	−337 999
1600	97.48	189.0	119 103	−356 589
1700	100.3	195.0	128 985	−375 788
1800	104.5	200.8	139 214	−395 579
1900	110.5	206.6	149 945	−415 951
2000	118.7	212.5	161 380	−436 905
2100	129.7	218.5	173 772	−458 454
2200	143.8	224.9	187 417	−480 621
2300	161.6	231.6	202 657	−503 443

us to meet condition $\sum_{i=1}^{m} \alpha_i = N_{\text{atoms}}$ approximately, and improved the limit behavior of function $C_p(T)$ when $T \to 0$ K. A simplified thermodynamic model with two Einstein functions and a polynomial can be used when T = 200–2000 K. It produces physically correct heat capacities when extrapolated to high and low temperatures, along with accurate values of $C^\circ_{p,298.15}$, $S^\circ_{298.15}$, and $H_T - H_{298.15}$. Its advantages over the polynomial model of [2] are half the number of parameters, no piecewise specified functions, and physically correct behavior when extrapolated to low temperatures.

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CONFLICT OF INTEREST

The author declares he has no conflicts of interest.

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